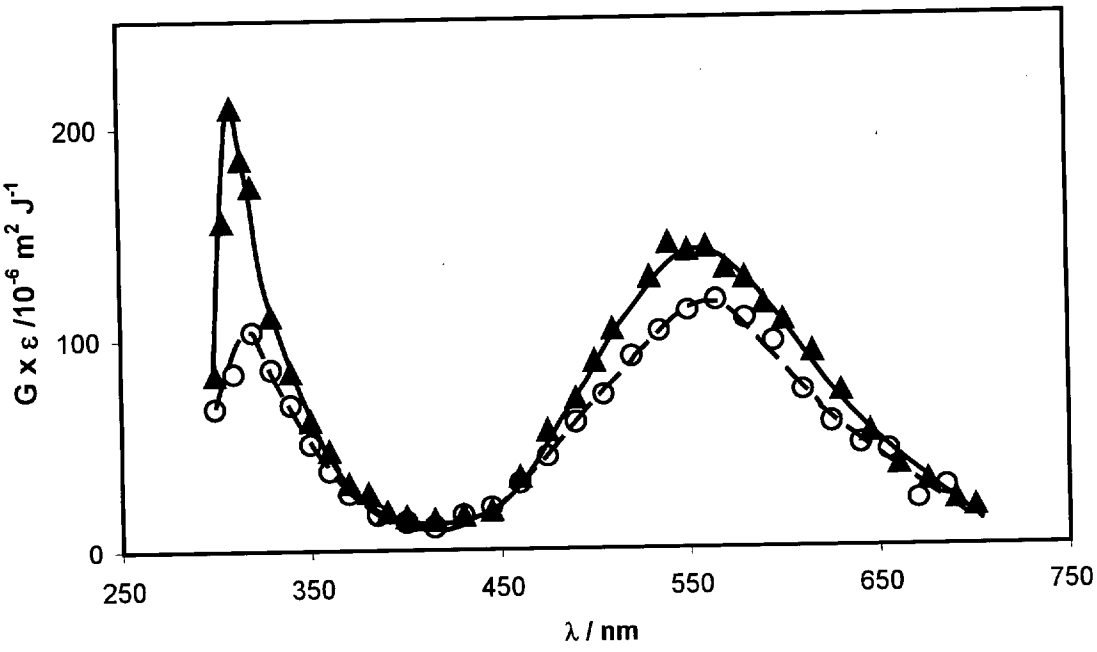

Figure 1S: Transient absorption spectra obtained in N_2O saturated aqueous solutions of 2-amino-4,6-dimethyl pyrimidine (ADMP) (1×10^{-3} mol dm^{-3}) at 2.5 μs after the pulse at pH 6 (O) and 10.4 (▲) (dose per pulse = 15 Gy).

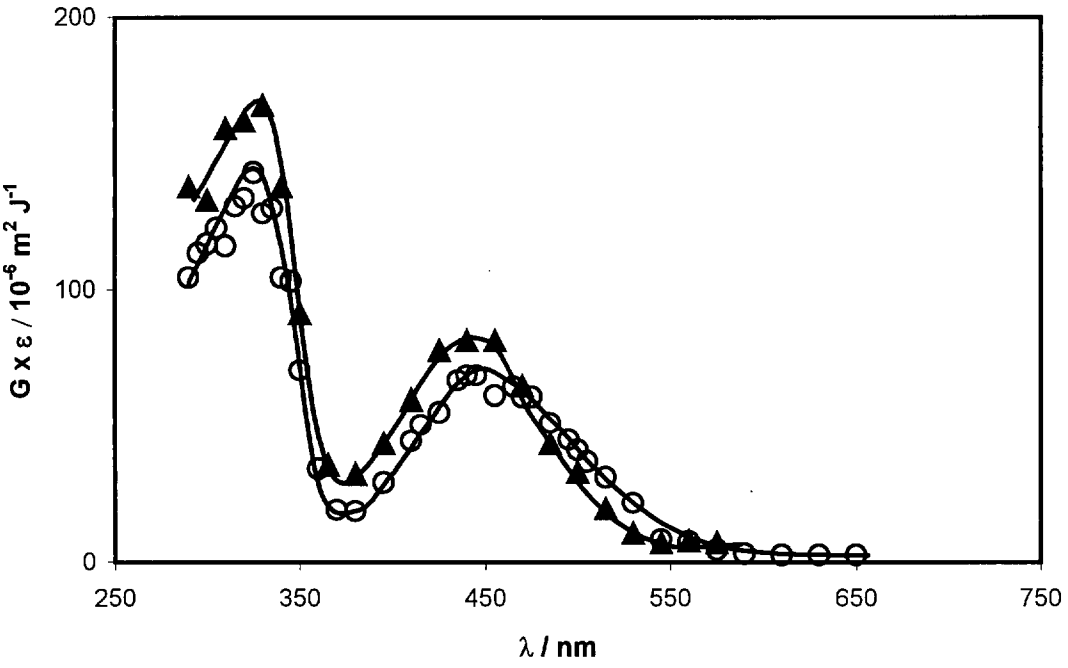

Figure 2S: Transient absorption spectra obtained in N_2O saturated aqueous solutions of 2,4-dimethyl-6-hydroxy pyrimidine (DMHP) (1×10^{-3} mol dm^{-3}) at 2 μs (O) after the pulse at pH 6 and 3 μs (▲) after the pulse at pH 10.4 (dose per pulse = 15 Gy).

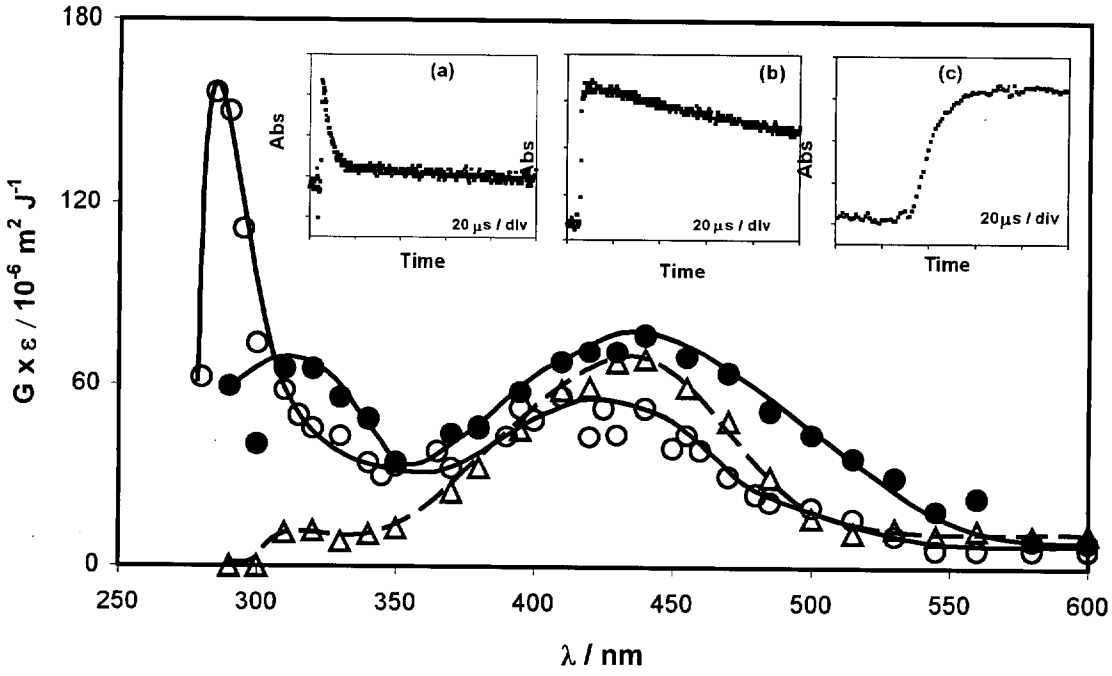

Figure 3S: Transient absorption spectra obtained in N_2O saturated solutions of 6-methyl uracil (MU) (1×10^{-3} mol dm^{-3}) at 1.5 µs after the pulse at pH 6 (O), at 2 µs (•) and 40 µs (Δ) at pH 10.4 (dose per pulse = 15 Gy) Inset: intermediate trace obtained at (a) 310 nm and (b) 440 nm at pH 10.4, (c) the $TMPD^{\bullet+}$ build-up at 565 nm obtained with MU (2×10^{-3} mol dm^{-3}) in presence of TMPD (5×10^{-5} mol dm^{-3}) at pH 10.4 (dose per pulse = 5 Gy).

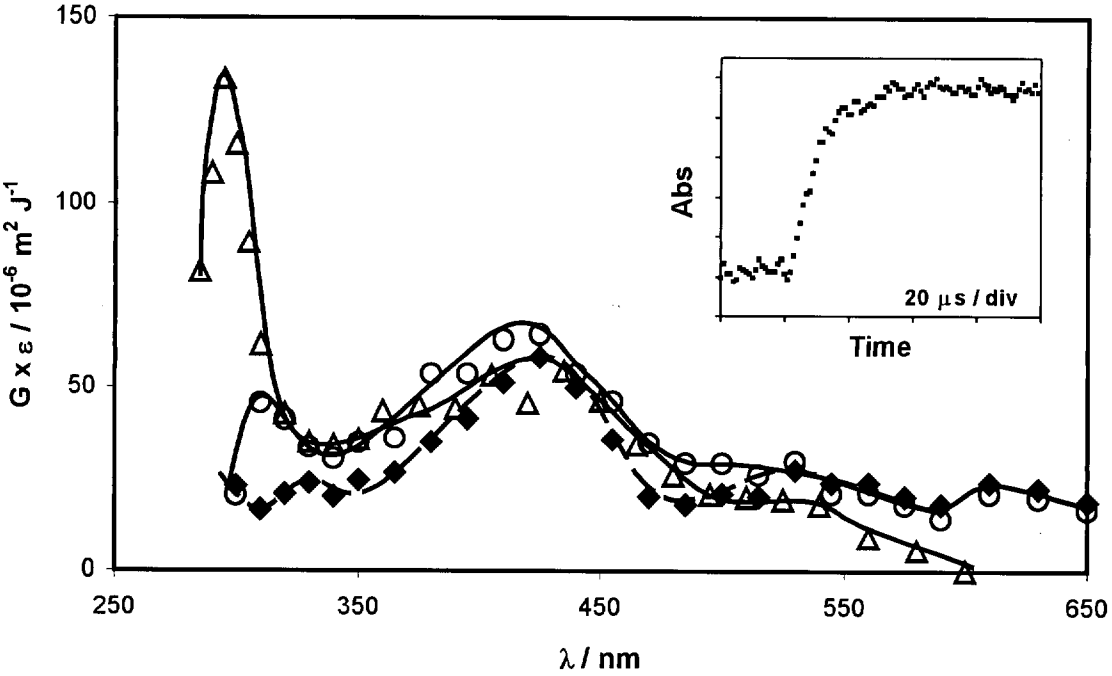

Figure 4S: Transient absorption spectra obtained in N_2O saturated solutions of 5,6-dimethyl uracil (DMU) (1×10^{-3} mol dm^{-3}) at 1 μs (Δ) after the pulse at pH 6, 3 μs (O) and 85 μs (◆) after the pulse at pH 10.4 (dose per pulse = 15 Gy). Inset: the $TMPD^{\bullet+}$ build-up at 565 nm obtained with DMU (2×10^{-3} mol dm^{-3}) in presence of TMPD (5×10^{-5} mol dm^{-3}) at pH 10.4, (dose per pulse = 5 Gy).

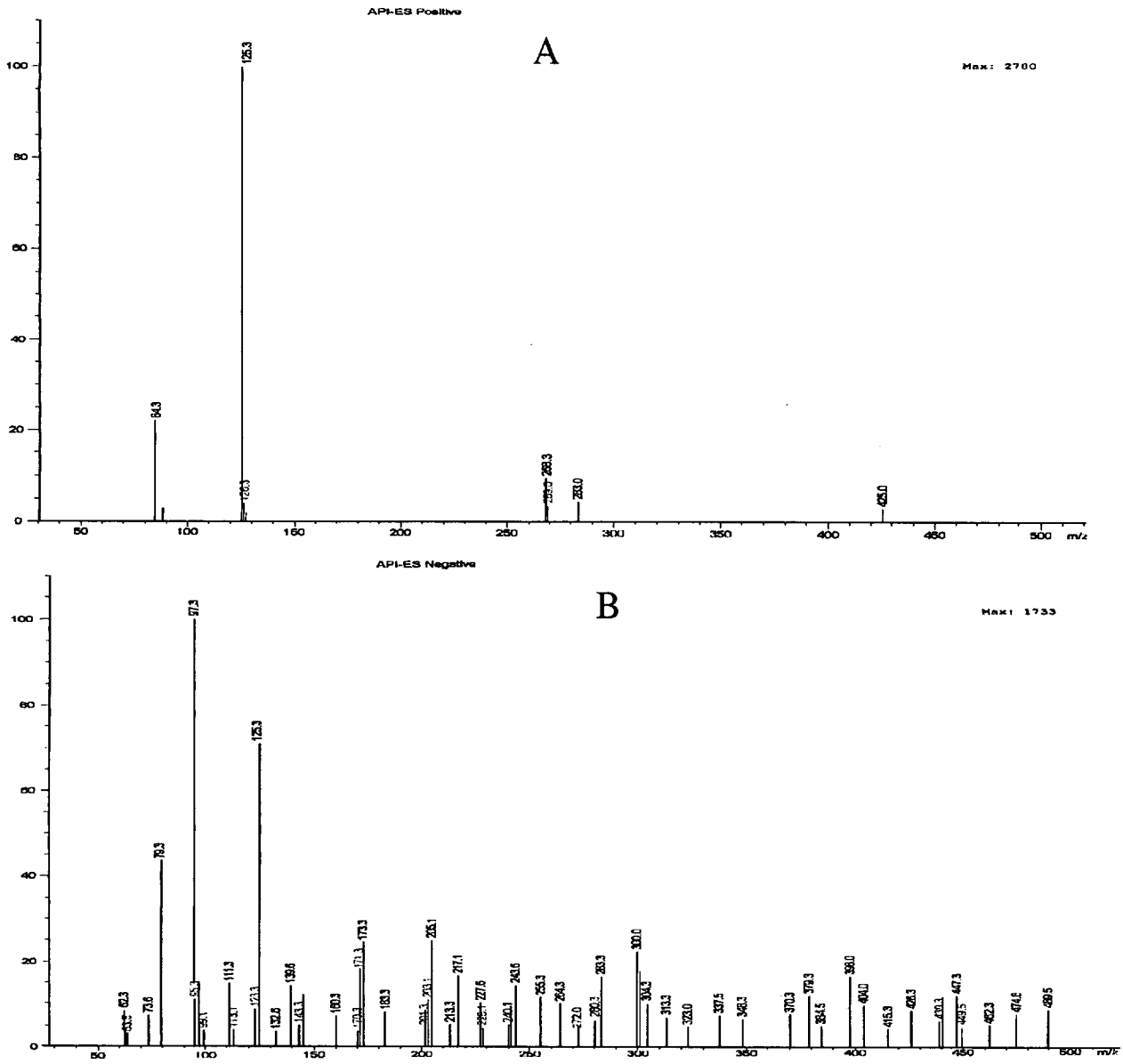

Figure 5S: Typical electrospray mass spectra obtained from a chromatographic peak obtained for the radiolysis of DMHP (10^{-3} mol dm^{-3}) saturated with N_2O at pH 6 (eluent: water). (**A**) positive ionisation mode, retention time Tr = 1.9 min. The signal at m/z = + 125 is assigned to 6-hydroxy-2,4-dimethyl pyrimidine (DHMP) and m/z = + 283 to bis(5-hydro-5,6-dihydro-2,4-dimethyl pyrimidine-6yl) (the product **o**); (**B**): negative ionisation mode, retention time Tr = 1.2 min. The signal at m/z = - 125 is assigned to 5,5-dihydro-6-hydro-6-hydroxy-2,4-dimethyl pyrimidine (the product **s**). The strong signal with m/z = -97 corresponds to HSO_4^- used in the buffer. The other products included in table 4 were obtained by scanning other regions of the HPLC chromatogram.